ACCESS VIII COLLOQUIUM

Yellowstone National Park, Wyoming
September 1 - 4, 2005

PROGRAM

Jointly Sponsored by:
U.S. Department of Energy
National Aeronautics and Space Administration
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ACCESS VIII COLLOQUIUM

AGENDA

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Thursday, September 1

Light Dinner (Mammoth Hot Springs Hotel*) . . . . 7:00 - 9:00 p.m.

Friday, September 2

Breakfast . . . . 7:30 a.m.

Introductory Remarks . . . . 8:30 a.m.

lenny Newman, Chair, ACCESS VIII Colloquium

SESSION CHAIR - Bruce Doddridge, NASA

ACCESS Presentations . . . . 8:50 a.m.

James Allan – Intensive Measurements of Aerosols at a Fixed, Ground-Based Site, Closure Studies and Applicability to Atmospheric Science

Rebecca Anderson – Carbon Kinetic Isotope Effects in the Gas-Phase Oxidations of Nonmethane Hydrocarbons by Hydroxyl Radicals and Chlorine Atoms

Roya Bahreini – Measurements of Secondary Organic Aerosol (SOA) Formed in Oxidation of Cycloalkenes, Terpenes, and m-xylene using an Aerodyne Aerosol Mass Spectrometer

Patrice Bell – Kinetics Study of the Reaction $OH + NO_2 + Air \rightarrow Products$

Christopher Cappa – Isotope Fractionation of Water During Evaporation Without Condensation

Coffee Break 10:30 a.m.

SESSION CHAIR - Erik Hintsa, NSF

ACCESS Presentations . . . . 11:00 a.m.

Ann Marie Carlton – SOA Production from Isoprene: Aqueous-Phase Mechanisms

Serena Chung – Equilibrium Climate Impact of Anthropogenic Black Carbon and Effect of Morphology on Lifetime and Radiative Forcing

Daniel Cohan – Atmospheric Science in the Public Realm

Juliane Fry – Kinetics and Spectroscopy of HOONO

Lunch . . . . 12:30 p.m.

SESSION CHAIR - Lenny Newman, BNL

Agency Presentations . . . . 1:30 p.m.

DOE	Steve Schwartz
NASA	Bruce Doddridge
NOAA	Fred Fehsenfeld
NSF	Eric Hintsa

SESSION CHAIR - Fred Fehsenfeld, NOAA

ACCESS Presentations . . . . 2:30 p.m.

Colette Heald – Asian Combustion Sources and Transpacific Transport: An Integration of Satellite and In Situ Observations with Global Models

Pramod Kulkarni – A New Electrical Mobility-based Aerosol Size Spectrometer for Fast Measurement of Aerosol Size Distributions

Nicholas Meskhidze – The Possible Role of Air Pollution in Dust-Fe Mobilization and Its Implications to Global Carbon Cycle

Coffee Break . . . . 3:30 p.m.

ACCESS Presentations . . . . 4:00 p.m.

Dylan Millet – Oxygenated Organic Gases In The Atmosphere

Benjamin Murray – The Formation of Cubic Ice Under Conditions Relevant for the Earth's Atmosphere

Shelley Pressley – Isoprene Flux Measurements Using Eddy Covariance and Disjunct Eddy Accumulation

Suresh Raja – Transport and Kinetics of Aromatics Vapors into Micro-Sized Droplets: With Applications to Atmospheric Chemistry

Adjourn . . . . 5:30 p.m.

Dinner . . . . 7:00 p.m.

Saturday, September 3

Breakfast . . . . 7:30 a.m.

SESSION CHAIR - Steve Schwartz, DOE

ACCESS Presentations . . . . 8:30 a.m.

Robyn Schofield – The Retrieval of Effective Radius by Combining Microwave and Near Infrared Observations made at Barrow, Alaska

Jay Slowik – Inter-Comparison of Instruments Measuring Black Carbon Content and Optical Properties of Soot Particles

Amy Sullivan – Isolation and Characterization of Fine Particle Carbonaceous Aerosols Soluble in Water using Solid Phase Extraction and Size-Exclusion Chroomatography

Brett Taubman – Summer Hot, Summer Not: Emissions, Transport, and Trends of Ground Level Ozone over the Mid-Atlantic U.S.

Timothy VanReken – Laboratory Measurements of Biogenically-Induced Particle Formation and Growth

Coffee Break . . . . 10:10 a.m.

ACCESS Presentations . . . . 10:30 a.m.

Erik Velasco – Measurement of Urban Trace Gas Emissions Using Micrometeorological Techniques: A New and Valuable Tool for Improving Air Quality Management

Yuxuan Wang – Emissions from China: Implications for the Regional and Global Environment

Dan Zhang – Laboratory Investigation of Physical and Optical Properties of Soot-Containing Aerosols

Ke "Max" Zhang – The Unusual Suspect: Environmental Ultrafine Particles

Bus Excursion to Old Faithful Inn** (Box Lunch Provided) . . . . . . 12:30 p.m.

Dinner at Old Faithful Inn . . . . 7:00 p.m.

Sunday, September 4

Breakfast . . . . 7:30 a.m.

Old Faithful Inn (Box Lunch Provided)

Excursion to Big Sky Resort . . . . 9:30 a.m.

Arrive at Big Sky Resort . . . . 5:00 p.m.

*Mammoth Hot Springs Hotel (9/01 - 9/03/2005)
**Old Faithful Inn (9/03- 9/04/2005)

24-hour phone number for any location within Yellowstone National Park is 307-344-7901. If someone needs to reach you, they should give your location (hotel) and your name to be connected to the right hotel.

ACCESS VIII COLLOQUIUM

ABSTRACTS

Intensive Measurements of Aerosols at a Fixed, Ground-Based Site, Closure Studies and Applicability to Atmospheric Science.

James Allan

It is universally accepted that aerosols remain an important area of study in many aspects of atmospheric science, ranging from health effects to global climate. Many of the advances in our understanding continue to be derived from the many measurements of atmospheric particles that have been performed over the years in a variety of locations worldwide. The quality and depth of such information continues to improve with newer and more advanced equipment and analytical techniques becoming available. Of particular current interest is the organic fraction of the aerosol, which while accounting for a large fraction of the total particulate matter, there is little known of the explicit composition, with existing analytical techniques accounting for a small fraction of the positively identified chemical species. Little is also known about exactly how much this fraction affects the behaviour of the aerosols and their impacts on larger issues such as climate. Much work is currently being performed to investigate and quantify the composition, sources, processes and effects of this fraction.

One such intensive field study, the Chebogue Point (Nova Scotia) deployment as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) programme, will be the main focus of this presentation. A suite of instrumentation from a number of groups was deployed, which included a variety of in situ gas and aerosol phase measurements. Aspects studied included the inorganic and organic compositions of the gases and particles, using many instruments such as a differential mobility particle sizer, condensation particle counters, an aerosol mass spectrometer and online particle and gas phase gas chromatography-mass spectrometers. In addition to the composition, other properties of the aerosols were measured, including their optical properties (using nephelometers) and how they interacted with water vapour (using a hygroscopicity tandem differential mobility analyser and a cloud condensation nuclei counter). These properties are crucially important when considering how aerosols affect visibility, clouds, rainfall and climate. These measurements can then be linked to characterise the aerosols originating from various sources, depending on the air mass history.

The compositions of the aerosols during this particular campaign were very interesting, as vastly varying amounts of organic and inorganic species were detected and quantified, which could be linked to changes in the volatility and hygroscopicity of the particles. Distinct changes in the composition of the organic fraction were also noted, both in terms of the identifiable species present and the overall levels of oxidation.

The next stage in the analysis of these data comes when trying to advance our understanding of the mechanisms behind the hygroscopic and optical properties. In trying to accurately understand the underlying processes governing hygroscopicity, models have been developed to try to predict the growth and activation properties of the particles based on their composition and studies such as this are vital in validating these. When fully developed, these models should be able to provide accurate parameters to feed into relevant larger-scale applications such as global climate models.

Also of much importance is being able to understand how the composition and properties of the aerosols are modified by atmospheric processes such as mixing, photochemically-initiated reactions and interactions with cloud and fog. By carefully and systematically comparing sources, air mass histories and the suite of compositions from multiple platforms, insights into these mechanisms can be made.

Carbon Kinetic Isotope Effects in the Gas-Phase Oxidations of Nonmethane Hydrocarbons by Hydroxyl Radicals and Chlorine Atoms

Rebecca Anderson

Light nonmethane hydrocarbons (NMHC) play an important role in the troposphere as precursors for atmospheric pollutants such as ozone, carbonyls, organic nitrates and secondary organic aerosols. The measurement of stable carbon isotope ratios of NMHC has been shown to be a very useful tool for investigating both chemical and physical processes affecting NMHC. To interpret ambient stable carbon isotope measurements, knowledge of the isotopic fractionation associated with chemical removal mechanisms is necessary. Reactions with OH radicals are the most important removal mechanism for most light hydrocarbons. Reactions with Cl atoms, though less important in the global troposphere, may account for significant hydrocarbon removal from arctic and marine atmospheres.

Measurements have been made of the stable carbon kinetic isotope effects (KIEs) for the reactions of a number of light alkanes, alkenes and aromatic hydrocarbons with OH radicals and Cl atoms. The method by which these measurements are made and a discussion of some key results will be presented, focusing primarily on comparisons between OH- and Cl-reaction KIEs. Using the measured KIEs, implications for both the atmospheric chemistry and the physical chemistry of these reactions are established and discussed.

Measurements of Secondary Organic Aerosol (SOA) Formed in Oxidation of Cycloalkenes, Terpenes, and m-xylene Using an Aerodyne Aerosol Mass Spectrometer

Roya Bahreini

The Aerodyne Aerosol Mass Spectrometer (AMS) was used to characterize physical and chemical properties of secondary organic aerosol (SOA) formed during ozonolysis of cycloalkenes and biogenic hydrocarbons and photooxidation of m-xylene. Estimates of “effective” density of SOA were determined by comparing mass and volume distributions from the AMS and Differential Mobility Analyzers; the values ranged in 0.64-1.45 g/cm^3, depending on the particular system. Dominant negative “delta” values of SOA formed during ozonolysis of biogenics indicates presence of terpene derivative structures or cyclic or unsaturated oxygenated compounds in the SOA. Evidence of acid-catalyzed heterogeneous chemistry is observed in the ozonolysis of a-pinene. Mass spectra of SOA formed during photooxidation of m-xylene exhibit features consistent with the presence of furandione compounds and nitro organics. This study demonstrates that mixtures of SOA compounds produced from similar precursors result in broadly similar AMS mass spectra. Thus, fragmentation patterns observed for biogenic vs. anthropogenic SOA may be useful in determining the sources of ambient SOA.

Kinetics Study of the Reaction $OH + NO_2 + Air \rightarrow$ Products

Patrice Bell[1], J.M. Nicovich[2], P.H. Wine[1,2]

The $OH + NO_2$ association reaction is one of the most important gas phase chemical transformations in atmospheric chemistry.

$$OH + NO_2 + Air \rightarrow HONO_2 + Air \quad (1a)$$
$$\rightarrow HOONO + Air \quad (1b)$$

Because reaction (1a) converts highly reactive HO_x and NO_x radicals into relatively unreactive nitric acid ($HONO_2$), models of urban air quality are more sensitive to the rate coefficient for this reaction (k_{1a}) than to any other single rate coefficient. Reaction (1a) also plays an important role in controlling radical levels in low temperature environments like the upper troposphere and lower stratosphere. Because of its importance in atmospheric chemistry, the $OH + NO_2$ reaction has been studied many times over the last 3 decades. Nonetheless, uncertainties in both the overall rate coefficient for OH removal ($k_1 \equiv k_{1a} + k_{1b}$) and the temperature and pressure dependence of the $HONO_2$ and HOONO product yields remain undesirably high. Peroxynitrous acid (HOONO) is a relatively weakly bound chemical species that is expected to dissociate to HO_2 + NO relatively rapidly in all but the coldest atmospheric environments. Hence, unlike reaction (1a), reaction (1b) is probably not a sink or long-term reservoir for HO_x and NO_x radicals in most atmospheric environments.

We are employing a laser flash photolysis – pulsed laser induced fluorescence technique to make high accuracy measurements of k_1 as a function of temperature (220 – 320 K) and pressure (20 – 800 Torr). The improvement over earlier work in our approach is the use of sensitive multipass absorption spectroscopy to quantitatively measure the NO_2 concentration both upstream and downstream from the reaction cell in the flowing gas mixture that contains NO_2, air, and a photolytic source for OH (H_2O_2 or $HONO_2$). This approach allowed us to make the most accurate measurements available of temperature-dependent rate coefficients for the key stratospheric reaction $O + NO_2 \rightarrow NO + O_2$ [*].

Attempts are also being made to directly observe the equilibration kinetics of reaction (1b) in order to obtain an estimate of the temperature dependence of the HOONO unimolecular decomposition rate in air; these results will be presented if completed by the time of the conference.

References:

* E.G. Estupinan, J.M. Nicovich, P.H. Wine, J. Phys. Chem. A 105, 9697-9703 (2001).

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Isotope Fractionation of Water During Evaporation Without Condensation

Christopher Cappa

The microscopic events engendering liquid water evaporation have received much attention over the last century, but remain incompletely understood. We present measurements of isotope fractionation occurring during free molecular evaporation from liquid microjets and show that the isotope ratios of evaporating molecules exhibit dramatic differences from equilibrium vapor values, strong variations with the solution deuterium mole fraction, and a clear temperature dependence. These results indicate the existence of an energetic barrier to evaporation and that the evaporation coefficient of water is less than unity. These new insights into water evaporation will help to improve our understanding of the processes that control the formation and lifetime of clouds in the atmosphere.

SOA Production from Isoprene: Aqueous-Phase Mechanisms

Annmarie G. Carlton[1], Katye Altieri[2], Sybil Seitzinger[2] and Barbara J. Turpin[1]

Glyoxal and methylglyoxal are water-soluble gas-phase oxidation products of isoprene and aromatic compounds. Lim et al., (2005) predicted that aqueous-phase oxidation of these compounds in cloud droplets produces glyoxylic and oxalic acid. These products remain, in part, in the particle phase after droplet evaporation. The result is SOA formation through cloud processing. Lim et al. (2005) estimated this process contributes 1.6 Tg yr^{-1} to global biogenic SOA production.

In this work, laboratory experiments were conducted to test and refine the mechanistic model used by Lim et al. (2005). Batch photochemical aqueous-phase oxidation experiments were conducted with hydrogen peroxide plus glyoxal or methlyglyoxal in 1 liter borosilicate reaction vessels with a monochromatic UV source (254 nm). Control experiments were conducted 1) without UV and 2) without hydrogen peroxide. Time series samples were taken over one hour at pH values typical of cloud and fog droplets. Samples were analyzed by high performance liquid chromatography (HPLC) and electro-spray ionization-mass spectrometry (ESI-MS) for precursors and products. Results are largely in agreement with Lim et al. (2005), showing that products of aqueous-phase photooxidation include oxalic, glyoxylic, pyruvic, acetic and formic acids. In addition, evidence was found for the formation of several carboxylic acid dimers. This evidence is presented in a companion paper (Altieri et al.). The presence of dimers suggests that SOA formation is greater than that predicted by Lim et al (2005). Experimental results were used to further elucidate the products of the aqueous-phase oxidation pathways and to improve our understanding of in-cloud SOA formation pathways. Yields and implications for in-cloud SOA formation will be discussed.

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Equilibrium Climate Impact of Anthropogenic Black Carbon and Effect of Morphology on Lifetime and Radiative Forcing

Serena H. Chung[†], John H. Seinfeld[‡], Laura H. van Poppel*, Heiner Friedrich*, Jacob Spinsby*, and Peter R. Buseck*

The equilibrium climate effect of direct radiative forcing of black carbon (BC) is examined by 100-year simulations in the Goddard Institute for Space Studies General Circulation Model II-prime with a mixed-layer ocean model. Anthropogenic BC is estimated to raise globally- and annually-averaged equilibrium surface air temperature by 0.20 to 0.37 K depending on whether BC is externally- or internally-mixed with present-day level of sulfate aerosol, indicating that the mixing state of BC contributes to significant uncertainty in the climate response. The predicted temperature increase is greater in the Northern Hemisphere than in the Southern Hemisphere by almost a factor of 3. For both externally- and internally-mixed BC, the estimated climate sensitivity is 0.6 K^{-1} W m^2, indicating a linear relationship between forcing and global mean surface air temperature response. The estimated climate sensitivity is about 30% less than that of doubled CO_2 forcing and similar to that of anthropogenic ozone forcing. Even though the predicted direct radiative forcing and climate sensitivity of BC is less than those of CO_2, climate impact of BC can be more important at the regional level. In addition, direct radiative forcing of BC is predicted to change of precipitation patterns in the tropics, leading to a northward shift of the intertropical convergent zone. The change in precipitation pattern is not predicted to alter the global burden of BC significantly because the change occurs predominantly in regions removed from BC sources.

Due to computational limitations and lack of knowledge about BC morphology, modeling studies have generally considered BC to consist of spherical particles. In reality, BC particles consist of smaller particles that aggregate into clusters having highly irregular and complex morphology. The morphology of BC particles has important implications for its atmospheric lifetime because it affects the rate by which the particles are coated with hydrophilic material. Morphological results obtained from electron tomography indicates that assumption of spherical geometry leads to underestimating of BC lifetime by up to 70%, which in turn leads to underestimation of direct radiative forcing by about 40%.

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Atmospheric Science in the Public Realm

Daniel Cohan

Atmospheric science is continually refining human understanding of the photochemical, dynamic, and climatological processes that govern air quality. But as state and local air protection agencies work to attain air quality standards, atmospheric science is just one of the myriad of practical, political, and economic realities that shape the development of sensible strategies. This talk will examine the extent to which atmospheric science is serving the needs of air quality planning at the state and local levels and outline opportunities for more closely integrating atmospheric modeling and observations into those efforts.

Over the years, advances in atmospheric science have strongly shaped attainment efforts and greatly enhanced their cost-effectiveness. For example, recognition of the role of abundant biogenic isoprene emissions has led southeastern states to shift their control focus from hydrocarbons to nitrogen oxides. However, full incorporation of atmospheric science into attainment planning has been hindered by several factors, including (1) lack of sufficient training, library resources, and scientific community interaction among agency personnel, (2) regulatory mandates and a litigious environment that create a tension between applying the most scientifically valid and the most readily approvable methods, and (3) a paucity of atmospheric science literature that directly addresses the needs of attainment planning. With dozens of regions now confronting multi-pollutant attainment dilemmas for ozone, particulate matter and regional haze, the need for atmospheric science to effectively inform air quality planning has never been greater. An integrated framework will be presented by which atmospheric sensitivity analyses and assessments of observational data can be linked with economic and epidemiological considerations to help states develop strategies that are both more cost-effective and more likely to result in actual attainment of air quality standards.

Kinetics and Spectroscopy of HOONO

Juliane L. Fry,[1] Sergey A. Nizkorodov,[2] Anne B. McCoy,[3] Joseph S. Francisco,[4] Andrew K. Mollner,[1] Brian J. Drouin,[5] Mitchio Okumura[1] and Paul O. Wennberg[1]

We have studied the kinetics and vibrational and rotational spectroscopy of peroxynitrous acid (HOONO). HOONO is a weakly-bound isomer of nitric acid produced in the OH + NO_2 reaction. The OH + NO_2 reaction is the major sink of both HOx (OH + HO_2) and NOx (NO + NO_2) families of radicals, important reactants in polluted air. The short thermal lifetime of HOONO makes it a temporary reservoir of OH and NO_2 rather than a permanent sink. Thus, understanding the extent and kinetics of HOONO formation is crucial to evaluating the OH + NO_2 reaction and the atmospheric concentrations of OH and NO_2. Laboratory studies apply spectroscopic techniques to study HOONO formation, and hence an understanding of HOONO spectroscopy is an essential foundation. We have investigated the spectroscopy of the HOONO first OH stretch overtone experimentally, using action spectroscopy and cavity ringdown spectroscopy, and theoretically, with two-dimensional coupled OH stretch – torsion models. We have also investigated the isomerization kinetics, both experimentally and with the statistical master equations method. In our lab, two conformers of HOONO are distinguished based on their differing time and temperature behavior, and assigned as cis-cis and trans-perp HOONO. The isomerization from the less stable trans-perp HOONO to cis-cis HOONO is observed directly in the range 223 - 238 K to determine the isomerization barrier of 33 ± 12 kJ/mol. Statistical calculations are consistent with the experimental measurement. These studies indicate that the only atmospherically relevant conformer is cis-cis HOONO. A direct absorption cavity ringdown spectrum of the first OH overtone region of cis-cis HOONO is measured for comparison to the action spectrum. The complex spectroscopy of the cis-cis HOONO first OH overtone region is then elucidated using a two-dimensional OH stretch – torsion coupling model, which accurately predicts the major features in both the absorption and action spectra of cis-cis HOONO. With this model, we are able to assign the major features in the cis-cis HOONO overtone spectrum and draw conclusions relevant to measurement of the branching ratio of HOONO to HNO_3, the quantity of importance in atmospheric modeling. In addition, we have studied the rotational spectroscopy of the atmospherically relevant cis-cis conformer of HOONO in the 400-700 GHz region, assigning the spectrum and determining the dipole moment by Stark effect measurement. We hope this will allow a future measurement of the concentration of HOONO in Earth's atmosphere.

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Asian Combustion Sources and Transpacific Transport: an Integration of Satellite and in Situ Observations with Global Models

Colette Heald

Quantifying the continental outflow and intercontinental transport of air pollutants is one of the greatest challenges of atmospheric chemistry today. It is expected that the industrialization of Asia will be one of the major drivers for changes in atmospheric composition in the coming decades. Recent studies have suggested that transpacific transport of Asian pollution has significant implications for ozone and aerosol air quality in the United States. In my Ph.D. work, tropospheric observations from space were linked with in situ observations and 3-D models to examine the mechanisms and impact of the intercontinental transport of these pollutants as well as the magnitude of their emission.

Satellite observations of carbon monoxide (CO) from the Measurement of Pollution in the Troposphere (MOPITT) instrument were combined with measurements from the TRACE-P aircraft mission over the northwest Pacific, and with a global 3-D chemical transport model (GEOS-Chem), to examine Asian pollution outflow and its transpacific transport during spring 2001. Four major events of transpacific transport of Asian pollution were seen by MOPITT, in-situ platforms, and GEOS-Chem, indicating that satellites can be used to successfully monitor long-range pollution transport. One of these events was sampled by TRACE-P over the NE Pacific and this analysis demonstrates the first field observation of PAN decomposition driving ozone production in polluted plumes transported to the remote troposphere.

Inverse modeling techniques were employed to compare the constraints on Asian sources of carbon monoxide from MOPITT satellite observations, and aircraft observations from the TRACE-P mission. MOPITT observations provide greater information towards geographically disaggregating source regions within Asia in comparison to the aircraft observations, reflecting the ability of the satellite to observe all outflow and source regions. The MOPITT and TRACE-P observations are independently consistent in the constraints that they provide on Asian CO sources, where biomass burning emissions are much less than previously thought and emissions from small industrial coal facilities in China have been underestimated.

Recent observations of Asian aerosol pollution at sites in western North America have raised concern about possible air quality implications. The value of MODIS satellite observations for quantifying transpacific aerosol pollution transport, forecasting Asian pollution events at sites in the United States, and testing a CTM (GEOS-Chem) simulation of this process was explored. Most transpacific aerosol pollution events observed by MODIS in spring 2001 are associated with significant Asian sulfate enhancements simulated by the model at sites in the NW United States, occasionally exceeding 1 $\mu g m^{-3}$.

A New Electrical Mobility-based Aerosol Size Spectrometer for Fast Measurement of Aerosol Size Distributions

Pramod Kulkarni

Measurement speed of aerosol instruments deployed in aircraft-based field studies is critical in determining the spatial resolution of measurements. The state-of-the-art differential mobility analyzers (DMA) take 50s or more to characterize one size distribution resulting in substantial loss of spatial resolution. A new Fast Aerosol Mobility Size Spectrometer (FAMSS) has been developed for fast measurement of entire submicron aerosol size distributions (12nm-1000nm) in less than 100ms. In this electrical mobility based instrument, particles are first separated based on their mobility in a parallel-plate geometry, and are subsequently grown into large droplets along their trajectories in a supersaturation environment. A high speed CCD camera is used to record mobility-dependent particle positions and counts, which are then used to derive particle size and concentration. This eliminates the need for voltage scanning required in traditional scanning DMA techniques, and ensures significant increase in measurement speed and counting statistics. A theoretical framework has been developed to obtain the transfer function of the instrument that facilitates characterizing its ideal performance over a range of operating conditions. A prototype has been developed, and its performance, including sizing accuracy, measurement resolution, and counting efficiencies are characterized.

The sizing accuracy of the instrument was successfully characterized by measuring monodispersed aerosol classified with DMA, and Polystyrene Latex standards over the size range of 12 to 170 nm. Experimental results show that AMSS has a 100% counting efficiency for particles as small as 12 nm. The resolution of the AMSS, defined as $Z_p/(DZ_p)$, where Z_p is characteristic mobility and Z_p is full width at half height of transfer function, ranged from 5 to 14 for particle diameters over the entire measurement range. Experimentally determined resolution agreed well with that predicted by theory, though there was some deviation observed at high mobilities. AMSS is capable of measuring an entire submicron size distribution spectrum in less than 100ms, thereby offering a great advantage over the traditional scanning mobility techniques in aircraft-based field studies.

The Possible Role of Air Pollution in Dust-fe Mobilization and Its Implications to Global Carbon Cycle

Nicholas Meskhidze[1], Athanasios Nenes[1], and William Chameides[2]

For iron (Fe) contained in aeolian dust to act as a micronutrient for oceanic phytoplankton, some fraction of it must first be transformed (mobilized) into a form soluble in ocean water. Dust-Fe solubilization in deliquesced mineral aerosols can occur by the incorporation of SO_2 into the advecting dust plumes and subsequent acidification of the dust through heterogeneous SO_2 oxidation. The possible role of air pollution in dust-Fe mobilization and its implications to global carbon cycle are investigated in two contrasting studies conducted in: (i) subarctic North Pacific (where long-range advected Gobi-dust plumes travel over industrially developed cities of China and therefore have an ample opportunity to entrain high concentrations of anthropogenic air pollutants, i.e., SO_2) and (ii) subantarctic South Atlantic (with dust plumes from Patagonia advected over sparsely populated pristine areas). Both regions of the ocean are known as high-nitrate low-chlorophyll (HNLC) areas where net primary productivity is limited by the availability of iron. In the first study, model simulations are carried out for documented Gobi-desert storms that advected mineral dust to Fe-limited regions of subarctic North Pacific. The estimated change in phytoplankton population inferred from the model-calculated inputs of bioavailable Fe is consistent with the satellite-measured chlorophyll a concentrations, suggesting that air pollution from China may actually affect net primary productivity and the associated uptake of atmospheric carbon dioxide in surface waters North Pacific Ocean. By extension, air pollution controls in China which lowered SO_2 emissions might depress carbon uptake in these same waters. Contrasting North Pacific, model simulations for subantarctic South Atlantic suggest that the amount of SO_2 available to be mixed with dust plumes from Patagonia is not high enough to acidify mineral dust and solubilize dust-Fe into bioavailable form. Analysis of remotely sensed sea surface temperature, ocean chlorophyll a content, sea level pressure and model-derived atmospheric dust-Fe fluxes revealed that surface ocean productivity in subantarctic South Atlantic is likely controlled by oceanic sources through upwelling of nutrient-rich waters from the deep ocean, continental margins and the island's shell. To the extent that biological activity in this region plays an important role in the contemporary global carbon cycle, this result suggests that changes in the dust-Fe supply, without significant increase in sulfur sources (i.e., from volcanic activities), may not exert considerable influence on the drawdown of atmospheric CO_2 in South Atlantic Ocean.

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Oxygenated Organic Gases In The Atmosphere

Dylan Millet

Oxygenated organic gases account for the majority of the non-methane organic carbon in the atmosphere. Such species influence atmospheric radical cycling, secondary aerosol formation, and ozone chemistry. Our ability to model these compounds is plagued by fundamental uncertainties.
In this presentation we will provide new constraints on the budgets of formaldehyde, acetaldehyde, methanol and acetone, drawing on a synthesis of recent observations from aircraft and ground stations with 3D chemical transport model simulations.

In the case of formaldehyde, we also exploit recent aircraft measurements to evaluate the uncertainty and applicability of satellite measurements. Errors in model treatment of the formaldehyde vertical profile as well as aerosol and cloud effects result in an uncertainty of 46% (2 sigma) for an individual retrieval scene. We provide observational evidence that HCHO columns observed from space may be used as a specific proxy of surface biogenic emissions. Recent aircraft measurements of HCHO and related tracers enable new constraints on the formaldehyde production yield from isoprene oxidation: we estimate an average time-integrated molar yield of 1.6 over North America in summer.

The Formation of Cubic Ice under Conditions Relevant for the Earth's Atmosphere

Benjamin J. Murray, Daniel A. Knopf and Allan K. Bertram

An important mechanism for ice cloud formation in the Earth's atmosphere is homogeneous nucleation of ice in aqueous droplets, this process is generally assumed to produce hexagonal ice. However, there are scattered reports that the metastable crystalline phase of ice, cubic ice, may form in Earth's atmosphere. Using a novel experimental approach we have demonstrated that cubic ice forms when micrometersized pure water and aqueous solution droplets freeze homogeneously at cooling rates approaching those found in the atmosphere. In fact, cubic ice is the dominant product when droplets freeze at temperatures below approximately 190 K, which is the temperature range relevant for clouds that form in parts of the upper troposphere and polar stratosphere. If there were a significant fraction of cubic ice in some cold clouds this could increase their water vapour pressure and modify their microphysics. Under specific conditions the transient presence of cubic ice may lead to enhanced sedimentation and therefore dehydration of the tropopause region through the mass transfer from cubic to hexagonal ice particles, a process analogous to the Bergeron-Findeisen process in mixed phase liquid water – ice clouds.

Isoprene Flux Measurements Using Eddy Covariance and Disjunct Eddy Accumulation

Shelley Pressley[1], Brian Lamb[1], Hal Westberg[1], Gene Allwine[1], Andrew Turnipseed[2], Alex Guenther[2]

Quantifying biogenic hydrocarbon (BHC) emissions is important for understanding the role they play in tropospheric chemistry. Isoprene is a very reactive compound that affects the oxidative capacity of the atmosphere, which in turn determines the lifetime of numerous atmospheric constituents such as methane (CH4) and CO. The oxidation of isoprene leads to the production of peroxy radicals (RO2), which may lead to the formation of organic acids, or depending on the level of nitric oxides present, to either production or consumption of tropospheric O3.

BHC emissions, in particular isoprene, are predominantly driven by increases in temperature and solar radiation, and there can be significant variations in emissions from one hour to the next, and between days. To better understand the natural variability of isoprene emissions, eddy covariance isoprene flux measurements are being collected on a long-term basis. This long-term dataset, spanning from 1999-2005, provides a unique tool for validating biogenic emission inventories that are used as input into regional photochemical models. This long-term dataset will be presented and compared to the biogenic emission inventory system (BEIS3) model estimates.

Using isoprene as a compound of interest, the micrometeorological technique of disjunct eddy accumulation (DEA) was tested side-by-side with the direct eddy covariance (EC) technique. One week of DEA and EC hourly flux measurements will be presented, confirming the use of DEA to measure fluxes of other atmospheric compounds that, to date, has not been attainable.

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Transport and Kinetics of Aromatics Vapors into Micron-Sized Droplets: With Applications to Atmospheric Chemistry

Suresh Raja and Kalliat T. Valsaraj

In the natural process of wet deposition, gas-water interfaces play an important role in the transport of chemical contaminants in the atmosphere via fog, rain and cloud drops. Evidences from several other works point out deviations in gas-liquid partitioning as predicted by Henry's law. Uptake and mass transfer of benzene, naphthalene, and phenanthrene was chosen to study in a falling droplet train apparatus. Higher droplet-to-vapor partition constant (K_{DV}) was noted for diameters less than 200μm and was attributed to surface adsorption and accumulation. Mass transfer of phenanthrene was dependent on gas-phase diffusion and mass accommodation at the interface, while the mass transfer of benzene was dependent on liquid phase diffusion and mass accommodation. Mass accommodation coefficients showed a negative dependence on temperature, resulting in lower partitioning at higher temperatures.

In order to understand the influence of atmospheric oxidants such as ozone on mass transfer and uptake of organic vapors in water droplets, ozone was introduced into the modified droplet train apparatus. Ozone reacted with PAH vapor at the air-water interface, thereby decreasing the mass transfer resistance and increasing the rate of uptake of naphthalene into the droplet. A Langmuir-Hinshelwood reaction mechanism at the air-water interface satisfactorily described the surface reaction, where the surface reaction rate constant increased with decreasing droplet size. The presence of organic matter in the liquid phase resulted in a higher droplet-to-vapor partition constant due to both presence and absence of ozone in the reactor.

The Retrieval Of Effective Radius By Combining Microwave And Near Infrared Observations Made At Barrow, Alaska.

Robyn Schofield, John Daniel, Susan Solomon, Roy Miller, and Bob Portmann

The role that aerosols play in changing the radiative properties of clouds is uncertain, with even the sign of the forcing undetermined. The need for remotely sensing clouds is becoming more apparent with the desire to achieve a global estimate of the radiative forcing due to changes in clouds. A network of ground-based or satellite measurements are the most likely means for providing the high temporal and spatial resolution required to reduce some of the uncertainty that currently exists for global cloud properties.

A new technique of combining microwave and infrared spectroscopic measurements of liquid water path (LWP) and path integrated liquid water path (PLWP) respectively, to obtain effective radius information is outlined. Microwave measurements are made routinely as part of the Aerosol and Radiation Measurement (ARM) program, the errors of the microwave measurement are investigated and compared to the official ARM product. The infrared measurements are conducted using spectroscopic measurements made in the wavelength region between 900 and 1700 nm.

The effective radius of clouds is retrieved using an optimal estimation retrieval scheme that takes into account the measurements, their uncertainities, prior knowledge of the effective radius and its uncertainty. The technique is applied to ground-based observations of clouds made during September at Barrow, Alaska, 2004.

Inter-Comparison of Instruments Measuring Black Carbon Content and Optical Properties of Soot Particles

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Black carbon (BC) is the principal component of soot and it has a pronounced effect on both the optical properties and the nature of chemical and morphological transformations. The quantitative detection of black carbon within soot particles is a challenging measurement. Several techniques, based either on optical or thermal properties of soot particles, have been developed for measuring BC. During May 2005, a set of experiments was conducted in the Boston College laboratories to inter-compare the following recently developed instruments that measure black carbon content and optical properties of soot particles: an Aerodyne Aerosol Mass Spectrometer (AMS) coupled with a Scanning Mobility Particle Sizer (SMPS), two Single Particle Soot Photometers (SP2), a Multi-Angle Absorption Photometer (MAAP), and a Photoacoustic Spectrometer (PAS). The above techniques measure the black carbon content and optical properties of particles in real or near real-time as opposed to conventional filter techniques that require a significant delay between collection and analysis. An optical detection module in the AMS and a Scanning Electron Microscopy (SEM) sampling system were also employed to provide additional information.

The operating principles of the four techniques utilized to detect BC are as follows. In the AMS-SMPS combination, the SMPS provides the particle mobility diameter (a measure of particle volume and shape), while the AMS provides the particle vacuum aerodynamic diameter (which in addition to volume and shape, is also a measure of density) and the quantitative composition of the non-refractory (i.e. non-black carbon) components. Together these measurements provide the total particle mass. The BC content is then calculated by mass balance. In the SP2 instrument a laser pulse heats the particle. The intensity of the particle incandescence is related to the BC mass. In the MAAP instrument, particles are continually collected on a glass filter and the change in filter absorbance and reflectance is calibrated to yield the BC mass. Finally, in the PAS, particles are heated by controlled light absorption and a microphone measures the resulting pressure increase that yields the BC mass.

In these experiments the black carbon detection by the different techniques was studied with soot particles of controlled size, composition, and morphology. Both freshly generated (nascent) and processed soot particles were studied. Particles were processed by coating nascent particles with anthracene or oleic acid. The oleic acid-coated particles were also passed through a thermal denuder to evaporate the coating and flame-generated organics. For calibration, commercially produced black carbon spheres were studied. Finally, sampling of ambient particles above a busy street was performed for 48 hours.

At this point final inter-comparison awaits refinement of calibration for the individual instruments. However, even at this point it is evident that the BC measurements from all instruments agree to within a factor of 2. The final agreement is expected to be significantly better. Completed analyses of the inter-comparison experiments will be presented including results of the electron micrograph studies.

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Isolation and Characterization of Fine Particle Carbonaceous Aerosols Soluble in Water Using Solid Phase Extraction and Size-Exclusion Chromatography

Amy P. Sullivan

A two-step method has been developed and tested to isolate chemical fractions of the ambient organic aerosol based on chemical functional groups. In the first step, water-soluble organic carbon (WSOC) aerosols are extracted from integrated filters and separated into hydrophilic and hydrophobic fractions using XAD-8 resin. In the second step, size-exclusion chromatography (SEC) is used to chromatographically separate by organic functional groups the WSOC recovered hydrophobic and hydrophilic compounds. The hydrophobic fraction is separated into aromatic acids and phenols or compounds with similar hydrophobic properties and the hydrophilic fraction is delineated into short-chain aliphatic carboxylic acids, neutral compounds (i.e. saccharides), and organic bases. The fractions are quantified directly by Total Organic Carbon (TOC) analysis in both steps. The method has been calibrated with atmospherically relevant organic standards and confirmed by C-NMR (Carbon-Nuclear Magnetic Resonance) analysis.

Comparisons are made between SEC fractions from urban Atlanta summer, urban Atlanta winter, and biomass burning samples. In the summer, small-chain aliphatic and aromatic carboxylic acids account for 20% of the organic carbon (by carbon mass) and are correlated with each other (R^2=0.74), with hydrophilic neutrals (R^2=0.61), and with gaseous 24-hour averaged VOCs (Volatile Organic Compounds) expected from mobile sources (e.g. isopentane R^2=0.67). During the winter when the water-soluble fraction of organic carbon is much lower (~40%), the organic aerosol is more similar to biomass smoke with a higher relative abundance of neutral (i.e. saccharides) and phenolic compounds. Compounds expected from secondary organic aerosol formation from biogenic sources are not recovered by this method, but their upper limit may be estimated by difference.

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Summer Hot, Summer Not: Emissions, Transport, and Trends of Ground Level Ozone over the Mid-Atlantic U.S.

Brett Taubman

The regular occurrence of summertime ozone episodes in the eastern U.S. presents a hazard to both human and ecological health. Since 1985, emissions of NO_x and VOCs have decreased by ~27% and ~44%, respectively. However, the impact of changes in precursor species concentrations on ozone formation is non-linear. Therefore, it is difficult to determine with certainty whether these emissions reductions have been successful in reducing near-surface ozone. In this study, we investigated 20 y time series (1985-2004) of daily 1 h and 8 h average maximum summertime (JJA) ozone values from the Washington, D.C., Baltimore, MD, and Philadelphia, PA non-attainment areas. Whereas the summertime means of the daily 1 h and 8 h maximum values for the three areas show no trends over the 20 y period, the frequency of annual ozone violations has decreased in these in these areas over the same time frame. However, the meteorologically driven variability must first be removed from the ozone data before an accurate determination of impacts due to the emissions reductions can be made. A cluster analysis of daily, 48 h, 3-dimensional back trajectories beginning at 500 m from the Baltimore/Washington corridor and Philadelphia was used to characterize summertime meteorological and transport patterns into the region. The relative contributions of the meteorological factors embedded in the trajectory clusters and the daily maximum temperatures to the variability of the daily ozone maxima were determined using an Analysis of Covariance. The meteorologically driven variability was removed from the 20 y time series, allowing for a more accurate assessment of the impacts due to precursor emissions reductions on near-surface ozone.

Laboratory Measurements of Biogenically-Induced Particle Formation and Growth

Timothy M. VanReken, James N. Smith, Alex Guenther, Peter Harley, Jim Greenberg, and Thomas Karl*

A unique "biogenic aerosol facility" has been developed to promote the study of biogenic emissions and their influence on new particle formation and growth. The facility is comprised of two interconnected chambers: a biomass chamber and a reaction chamber. The biomass chamber is an open-ended PTFE bag that can be placed over a photosynthetically-active plant source (e.g., a young pine tree). This chamber is plumbed so that the accumulated VOC emissions from the plant can be passed to the reaction chamber. The reaction chamber is a one cubic meter PTFE bag with several sampling ports. For the experiments described here which focus on ozone chemistry, the chamber is kept dark by placing it in a light-tight stainless steel enclosure constructed for this purpose. In addition to controlling the VOC concentration within the reaction chamber by passing and/or recirculating clean air through the biomass chamber, additional equipment is in place to control the temperature, relative humidity, ozone concentration, and sulfur dioxide level; it is also possible to add seed aerosol to the chamber when desired. Measurement capabilities include trace gas measurements using Proton Transfer Reaction Mass Spectrometry (PTRMS) and various aerosol properties, including number concentration and size distribution, hygroscopicity, CCN activity, and composition. As a whole, this new facility represents a powerful tool for examining the mechanisms for biogenic secondary organic aerosol formation and growth in the atmosphere.

The capabilities of the biogenic aerosol facility are demonstrated by reproducing experiments in which pure monoterpene precursors are observed to form new particles in the absence of a seed aerosol. Additionally, a series of experiments is conducted exploring the dependence of new particle formation on the background concentrations of ozone, sulfur dioxide, and the VOCs emitted by the biomass sample (it has been proposed that sulfuric acid clusters, arising from the oxidation of sulfur dioxide, are a prerequisite for new particle formation). These initial experiments focus on a single plant species whose emissions have previously been characterized; future studies will examine additional species. These initial experiments will be discussed, emphasizing the dependence of the resultant aerosol on the gas-phase precursors.

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Measurement of Urban Trace Gas Emissions Using Micrometeorological Techniques: a New and Valuable Tool for Improving Air Quality Management

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Direct measurements of emissions of trace gases that include all anthropogenic and biogenic emission sources in urban areas are a missing requirement to evaluate emission inventories and constrain current photochemical modeling practices. As part of the MCMA-2003 field campaign we demonstrated the use of eddy covariance systems coupled with fast-response sensors to measure urban fluxes of selected volatile organic compounds (VOC) and CO_2 from a neighborhood of Mexico City, where the spatial variability of emissions sources, surface cover and roughness is high. The CO_2 flux measurements showed that the urban landscape is a net source for CO_2 with similar diurnal patterns and magnitudes to those observed in US or European cities. VOC and CO_2 fluxes exhibited a clear diurnal pattern with a strong relationship to vehicular traffic. Fluxes of olefins, methanol, acetone, toluene and C_2-benzenes were measured and compared with the local gridded emission inventory. Recent photochemical modelling results suggest that VOC emissions are significantly underestimated in Mexico City, but for the olefin class, toluene, C_2-benzenes, and acetone fluxes measured in this work, the results show general agreement with the gridded emission inventory. While these measurements do not address the full suite of VOC emissions, the comparison with the inventory suggests that other explanations may be needed to explain the photochemical modelling results.

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Emissions from China: Implications for the Regional and Global Environment

Yuxuan Wang

Rapid industrial development over the past 20 years in East Asia and specifically in China has resulted in unprecedented growth in emission of important trace gases with implications for both the global and regional environment. An important objective of this research is to define the nature and extent of these emissions. Observations of CO and reactive nitrogen (NO_y) from the TRACE-P aircraft mission, and from two Chinese ground stations (Hong Kong and Lin An) during spring 2001 are used in conjunction with an optimal estimation inverse model to constrain emissions of CO and NO_x from Asia. The inversion analysis implied that bottom-up results for emissions of CO and NO_x from China should be increased by 43% and 47%, respectively. Large adjustments were required for emissions from central China. A posteriori estimates of emissions from biomass burning in Southeast Asia were found to be lower than a priori values, consistent with conclusions reached in other TRACE-P studies. An analysis of ratios for emission of CO relative to NO_x for different industrial sectors indicated that emissions of CO and NO_x attributed to industry and transportation may be underestimated in the bottom-up inventory for central China, while emissions from the domestic sector may be underestimated for south China. Results obtained in this study for the magnitude and spatial distribution of the missing source of CO are consistent with conclusions derived independently in an ongoing revision of ottom-up emissions for CO for the TRACE-P mission period.

The increase in NO_x emissions inferred for central China is too large, however, to be accommodated by any reasonable adjustment of sources from combustion of either fossil or biofuel. We proposed that the missing source of NO_x may be associated with microbially mediated decomposition of human and animal wastes associated with the agriculture/animal/human food chain and with extensive applications of chemical fertilizer. An examination of the contribution of the agriculture/animal/human food chain to the global budgets of N_2O and NO_x is conducted. More than 220 Tg N are processed annually through the global agriculture/animal/human food chain, with over 50% contributed by domestic animals. Review of the microbial processes governing emissions of N_2O and NO_x suggests that aerobic denitrification, reduction of nitrite (formed in the first stage of nitrification) by nitrifying bacteria under low oxygen conditions, is an important source not only of global N_2O but also of NO_x. Yields of both species are enhanced at low oxygen, with the ratio of NO to N_2O (mole N / mole N) greater than 1 and increasing with decreasing levels of O_2. A simple top-down method indicates a globally averaged yield of 2% for N_2O formed from nitrogen involved in this chain. It was shown that a yield of this magnitude can account not only for the contemporary budget of atmospheric N_2O but also for trends observed over the past 1000 years.

The associated microbial source of NO_x was estimated assuming a NO_x/N_2O ratio of 3, consistent with results from a variety of laboratory and field studies. This yield for NO_x is large enough to resolve the discrepancy between bottom-up estimates for emissions of NO_x from central China reported by Streets et al [2003] and values derived using the inverse, top-down, approach. The microbial source of NO_x is significant, particularly for large developing countries such as China and India, for which its contribution is comparable to that from fossil fuel.

Laboratory Investigation of Physical and Optical Properties of Soot-Containing Aerosols

Dan Zhang

Soot particles released from fossil fuels combustion and biomass burning have a large impact on the regional/global climate by altering the radiative properties of the atmosphere and by serving as cloud condensation nuclei (CCN). However, the exact forcing is affected by the mixing state of soot with other aerosol constituents, such as sulfuric acid. Despite the important role of soot and sulfuric acid in the atmosphere, our current understanding is very limited on their interaction mechanism, and the impact of mixing on the hygroscopic and optical properties of soot. In this work, experimental studies have been carried out focusing on three integral parts: (1) heterogeneous uptake measurements of sulfuric acid on soot using a low-pressure laminar-flow reactor coupled to ion drift-chemical ionization mass spectrometry (ID-CIMS) detection; (2) RH-dependent hygroscopic growth measurements of soot-H_2SO_4 mixed aerosols using a tandem differential mobility analyzer (TDMA) system; (3) study of the effect of H_2SO_4 mixing on the scattering and extinction coefficients of soot particles using a three-wavelength nephelometer and a multi-path extinction cell. Our results suggest that uptake of H_2SO_4 takes place efficiently on soot particles, representing an important route to convert hydrophobic soot to hydrophilic aerosols. The aging process has large impact on the hygroscopic and optical properties of soot, and aged soot particles in the atmosphere can potentially be an efficient source of CCN. The results will improve our ability to model and assess the soot direct and indirect forcing and hence enhance our understanding of the impact of anthropogenic activities on the climate.

The Unusual Suspect: Environmental Ultrafine Particles

K. Max Zhang

Air pollution causes more than 50,000 premature deaths per year in the U.S. alone. Even though the current national ambient air quality standard for particulate matters (PM) are mass-based, it is still not clear which attribute(s) of PM poses the greatest health risk. Increasing evidence from epidemiological studies has linked ultrafine (<100 nm) particles, which can deposit deeply into lungs and further make their way into blood streams, to negative respiratory and cardiovascular health effects. Motor vehicles are the major source of atmospheric ultrafine particles. Besides direct tailpipe emissions, nano-size particles can also be formed from exhaust dilution-induced nucleation. Understanding the emission and plume-processing of ultrafine particles from mobile sources is a crucial part of the ultrafine particle study.

We first analyzed the relevant atmospheric processes in the plume processing, and proposed a modeling structure simulating the aerosol chemistry and dynamics from tailpipe to ambient background. Next we modeled the data collected near highways in Los Angeles, CA, where dramatic emission profile changes have been observed. We concluded that the major driving force of this near-road dynamics is the interaction of turbulent dilution (either by moving traffic or atmospheric shear) and condensation/evaporation of volatile materials in the gaseous and particulate phases, and that the chemical compositions of exhaust particles change accordingly.

Due to their susceptibility to plume processing, the emission profiles of ultrafine particles become receptor-dependent. A clear definition is therefore needed. There are three types of emission profiles: tailpipe-level, road-level and grid-level. Residents living in communities far from freeways are exposed to grid-level emissions, while people living near or traveling on the freeways are exposed to road-level or even tailpipe-level emissions. Using concurrently measured carbon monoxide (CO) as a freeway dilution indicator and correlating roadside particle measurements to CO measurements, we have derived the receptor-dependent mobile emission factors at road and grid-level.

Our findings on mobile emissions have great implication on human exposure to exhaust pollutants. These indicate that people living in the vicinity of freeways are exposed to particle sizes and compositions that others are not, which will bring to regulators' attention issues that are important in planning further development close to freeways.